METHOD OF DETERMINING ERROR IN CALCU-
LATED PARAMETERS OF COMBUSTION PROCESS
RESULTING FROM ERROR IN THERMODYNAMIC
PROPERTIES OF INDIVIDUAL SUBSTANCES

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Wright-Patterson Air Force Base, Ohio

1 November 1974

FD/A002 11

DOCUMENT CONTROL DATA · R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Foreign Technology Division	UNCLASSIFIED
Air Force Systems Command	2b GROUP
U. S. Air Force	

3 REPORT TITLE

METHOD OF DETERMINING ERROR IN CALCULATED PARAMETERS OF COMBUSTION PROCESS RESULTING FROM ERROR IN THERMODYNAMIC PROPERTIES OF INDIVIDUAL SUBSTANCES

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Translation

5 AUTHOR(S) *(First name, middle initial, last name)*

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6 REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
1972	12	2

8a CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b PROJECT NO	FTD-HT-23-1939-74
c	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10 DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
	Foreign Technology Division
	Wright-Patterson AFB, Ohio

13 ABSTRACT

21, 20

(12)

DD FORM NOV 65 1473

i.

EDITED TRANSLATION

FTD-HT-23-1939-74   19 November 1974

CSP 73193384

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PARAMETERS OF COMBUSTION PROCESS RESULTING
FROM ERROR IN THERMODYNAMIC PROPERTIES OF
INDIVIDUAL SUBSTANCES

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English pages: 6

Source: Goreniye i Vzryv, Izd-vo Nauka, Moscow,
1972, pp. 435-438

Country of Origin: USSR

Translated by: Marilyn Olaechea
Requester: FTD/PDTN
Approved for public release;
distribution unlimited.

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А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	ъ	*ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	ь ь	*ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yë or ë.
The use of diacritical marks is preferred, but such marks
may be omitted when expediency dictates.

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RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

GREEK ALPHABET

Alpha	A	α	●	Nu	N	ν	
Beta	B	β		Xi	Ξ	ξ	
Gamma	Γ	γ		Omicron	O	o	
Delta	Δ	δ		Pi	Π	π	
Epsilon	E	ε	●	Rho	P	ρ	●
Zeta	Z	ζ		Sigma	Σ	σ	ς
Eta	H	η		Tau	T	τ	
Theta	O	θ	●	Upsilon	T	υ	
Iota	I	ι		Phi	Φ	φ	φ
Kappa	K	ϰ	κ	Chi	X	χ	
Lambda	Λ	λ		Psi	Ψ	ψ	
Mu	M	μ		Omega	Ω	ω	

METHOD OF DETERMINING ERROR IN CALCULATED PARAMETERS OF COMBUSTION PROCESS RESULTING FROM ERROR IN THERMODYNAMIC PROPERTIES OF INDIVIDUAL SUBSTANCES

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Kazan'

Thermodynamic calculation is broadly used to determine the parameters of the combustion process. Error in any parameter of the process ϕ, determined as a result of thermodynamic calculation, depends on:

a) the mathematical error of the calculation method;

b) error in the original data on the fuel (enthalpy and elementary composition of the fuel);

c) error from reference data on properties of individual substances - components of combustion products (enthalpy I_q^0, entropy S_q^0, and other properties of q-th substance).

Studied in the work is the effect of error from reference data on the properties of individual substances; errors of type a and b have already been discussed in the literature [1].

In the case of a constant elementary fuel composition (number of atoms of the i-th chemical element in a molecule of the fuel

$t_i = const$) any parameter of the combustion process ϕ may represent the function of enthalpy i and entropy s of the combustion products. The enthalpy and entropy in turn are determined by the composition of the mixture and by the thermodynamic properties of the individual substances I_q^0 and S_q^0. Consequently, error $\Delta\phi$ which develops as a result of errors in the thermodynamic properties of the individual substances can, in the final analysis, be expressed as ΔI_q^0 and ΔS_q^0.

The reference book [2] gives the following expressions for enthalpy I_q^0, the change in enthalpy $(H_T^0 - H_0^0)_q$, and entropy S_q^0 of the q-th substance:

$$I_q^0 = \Delta H^0 f_{293,\,q} + (H_T^0 - H_0^0)_q - (H_{293}^0 - H_0^0)_q; \tag{1}$$

$$(H_T^0 - H_0^0)_q = R_0 T^2 \left(\frac{\partial \ln \zeta_q}{\partial T} \right)_p; \tag{2}$$

$$S_q^0 = R_0 \ln \frac{Q_q}{N} + R_0 T (\partial \ln Q_q / \partial T)_p, \tag{3}$$

where Q_q is the statistical sum with respect to the states of the molecules; $\Delta H^0 f_{293_q}$ - the heat of formation.

As we see, errors ΔI_q^0 and ΔS_q^0 are determined by the errors of four quantities, which will henceforth be conditionally denoted as:

$$\omega_{qk} = \Delta H^0 f_{293,\,q}; \quad (H_{293}^0 - H_0^0)_q; \quad \ln \frac{Q_q}{N}; \quad \left(\frac{\partial \ln Q_q}{\partial T} \right)_p. \tag{4}$$

Consequently, the error of parameter ϕ for small error ω_{qk} is the linear functional for $\Delta\omega_{qk}$

$$\Delta\phi = \sum_q \sum_k \left(\frac{\partial\phi}{\partial\omega_{qk}} \right)_{x_i} \cdot \Delta\omega_{qk}, \tag{5}$$

where quantities $\Delta\omega_{qk}$ are determined by the reference data of [2]; α_i - the parameters which determine the form of the combustion process.

To calculate $\Delta\phi$ in the general case we must solve the problem

of linear programming, since for certain components $\Delta H^0 f_{293}$ are expressed through the enthalpy of key substances, and errors $\Delta(H^0_T - H^0_0)$ and $\Delta(H^0_{293} - H^0_0)$ are to a certain extent interrelated.

Let us obtain some general relationships for the derivatives $(\partial\phi/\partial w_{qk})_{\alpha1}$. As we know, the thermodynamic description of many processes in closed systems is based on the assumption that a certain function of state ψ (for example, the enthalpy of the fuel for isobaric combustion, entropy - for isentropic expansion) does not change during the process. For such cases any parameter of the combustion products ϕ may be represented by the functions

$$\left.\begin{aligned}\varphi &= \alpha(p,\ T,\ \omega_{qk}), \\ \varphi &= \beta(p,\ \psi,\ \omega_{qk}).\end{aligned}\right\} \tag{6}$$

After we have equated the total differential functions of α and β for p and $\psi=$const we get

$$\left(\frac{\partial\varphi}{\partial\omega_{qk}}\right)_{p,\psi} = \left(\frac{\partial\varphi}{\partial\omega_{qk}}\right)_{p,T} + \left(\frac{\partial\varphi}{\partial T}\right)_{p,\omega_q}\left(\frac{\partial T}{\partial\omega_{Hk}}\right)_{p,\psi}. \tag{7}$$

On the other hand, if we write the total differential of the function $\psi(p,\ T,\ \omega_q)$ for p and $\psi=$const, we get

$$\left(\frac{\partial T}{\partial\omega_{qk}}\right)_{p,\psi} = -\frac{\left(\frac{\partial\psi}{\partial\omega_q}\right)_{p,T}}{\left(\frac{\partial\psi}{\partial T}\right)_{p,\omega_q}}. \tag{8}$$

Thus, for partial derivatives of the thermodynamic parameters the following expression is valid:

$$\left(\frac{\partial\varphi}{\partial\omega_{qk}}\right)_{p,\psi} = \left(\frac{\partial\varphi}{\partial\omega_{qk}}\right)_{p,T} - \left(\frac{\partial\psi}{\partial\omega_{qk}}\right)_{p,T}\cdot\frac{\left(\frac{\partial\varphi}{\partial T}\right)_{p,\omega_q}}{\left(\frac{\partial\psi}{\partial T}\right)_{p,\omega_q}}. \tag{9}$$

Let us use formula (9) for the case of isobaric combustion, described by the equations

$$\left.\begin{aligned}p_k &= \text{const}, \\ i_k &= \text{const}\end{aligned}\right\}. \tag{10}$$

where the subscript "к" refers to parameters in the combustion chamber.

As a result we get:

for the temperature of the combustion products T_k

$$\left(\frac{\partial T_k}{\partial \omega_{qk}}\right)_{p,i} = \frac{1}{c_p}\left(\frac{\partial i}{\partial \omega_{qk}}\right)_{p,T} \quad (11)$$

for the molecular weight of the combustion products μ_k

$$\left(\frac{\partial \mu_k}{\partial \omega_{qk}}\right)_{p,i} = \left(\frac{\partial \mu_k}{\partial \omega_{qk}}\right)_{p,T} \quad \frac{\mu_k}{c_p T_k}(1-\alpha_p T_k)\left(\frac{\partial i}{\partial \omega_{qk}}\right)_{p,T} \quad (12)$$

for the number of moles of the q-th substance in the combustion products

$$\left(\frac{\partial n_q}{\partial \omega_{qk}}\right)_{p,i} = \left(\frac{\partial n_q}{\partial \omega_{qk}}\right)_{p,T} - \frac{1}{c_p}\left(\frac{\partial i}{\partial \omega_{qk}}\right)_{p,T}\left(\frac{\partial n_q}{\partial T_k}\right)_{p,\omega_q} \quad (13)$$

where α_p is the isobaric expansion coefficient; c_p - heat capacity at p=const.

The derivatives $(\partial i/\partial \omega_{qk})$ and $(\partial \mu_k/\partial \omega_{qk})$ are written as the result of differentiating known expressions [1]. For example, for enthalpy we have

$$\left(\frac{\partial i}{\partial \omega_{qk}}\right)_{p,T} = \frac{\sum_n n_n i_n^0\left(\frac{\partial \ln r_n}{\partial \omega_{qk}}\right)_{p,T} + n_q\left(\frac{\partial i_q^0}{\partial \omega_{qk}}\right)_{p,T}}{\mu_T M_T} - i\left(\frac{\partial \ln M_T}{\partial \omega_{qk}}\right)_{p,T} \quad (14)$$

where M_T is the number of moles in the fuel, giving us the equality of [1]

$$\left.\begin{array}{c} p = \sum n_q, \\ \left(\frac{\partial \ln \mu}{\partial \ln x}\right)_p = \left(\frac{\partial \ln M_T}{\partial \ln x}\right)_p \end{array}\right\} \quad (15)$$

where μ_T is the molecular weight of the fuel; x - any parameter.

To determine partial derivatives $(\partial \ln n_q/\partial \omega_{qk})_{p,T}$ and $(\partial \ln M_T/\partial \omega_{qk})_{p,T}$ we differentiate the system of equations for thermodynamic equilibrium [1] with respect to ω_{qk} at p and T=const.

As a result we get a closed equation system for calculating the derivatives:

$$\left(\frac{\partial \ln n_j}{\partial w_q}\right)_{p,T} - \sum_i a_{ij}\left(\frac{\partial \ln n_i}{\partial w_q}\right)_{p,T} = \delta_{jq} R_j + \delta_{iq} R_i; \qquad (16)$$

$$\sum_j a_{ij} n_j \left(\frac{\partial \ln n_j}{\partial w_q}\right)_{p,T} + n_i \left(\frac{\partial \ln n_i}{\partial w_q}\right)_{p,T} - B_i \left(\frac{\partial \ln n_T}{\partial w_q}\right)_{p,T} = 0; \qquad (17)$$

$$\sum_n n_n \left(\frac{\partial \ln n_n}{\partial w_q}\right)_{p,T} = 0, \qquad (18)$$

where δ_{jq} and δ_{ii} are the Kronecker symbols; i - atomic component; j - molecular component; quantities R_i and R_j are determined by differentiating the logarithm of the equilibrium constant, and are given in Table 1.

Table 1

	ΔH^0_{293}	$H^0_{298} - H^0_0$	$\ln \frac{Q}{N}$	$\left(\frac{\partial \ln Q}{\partial T}\right)_p$
R_i	$\frac{a_{ij}}{R_0 T}$	$-\frac{a_{ij}}{R_0 T}$	$-a_{ij}$	$\bullet$
R_j	$-\frac{1}{R_0 T}$	$\frac{1}{R_0 T}$	1	$\bullet$
$\left(\frac{\partial w^0_q}{\partial w_q}\right)_{p,T}$	1	-1	$\bullet$	$R_0 T^2$

The values of quantity Δw_{kj} can be selected on the basis of published data. For the calculations below the data of [2] were used along with materials from the 3rd edition of this handbook, which is being prepared.

We took errors $\Delta(\Delta H^0 f_{293_q})$ and $\Delta(H^0_{293} - H^0_0)_q$ directly from the tabulated data of [2]; error in Q/N was determined from the ratio

$$\Delta \ln \frac{Q}{N} = \frac{\Delta \phi^0_T}{R_0}. \qquad (19)$$

where ϕ^0_T is the reduced thermodynamic potential, whose error is given in [2].

To calculate errors $\Delta(\partial \ln Q/\partial T)_p$ we used the approximate estimate recommended in [2]

$$\Delta S_{\bullet}^{0} \approx (2 - 3)\Delta\Phi_{T_0}^{\cdot}. \tag{20}$$

Consequently, the greatest error equals

$$\Delta\left(\frac{\partial \ln Q}{\partial T}\right)_{p} = 4\,\frac{\Lambda\Phi_{r}^{\cdot}}{R_0 T}. \tag{21}$$

The presented method of estimating the errors in parameters $\Delta\Phi$ was used to determine errors ΔT_k and $\Delta\mu_k$, which arise in calculating the combustion process of several fuels. Characteristic quantities for relative errors $\delta T_k\%$ and $\delta\mu_k\%$ are given in Table 2 (pressure p_k - MN/m^2, α_{OH} - excess oxidant ratio).

Table 2

Fuel	α_{ox}	p_x	δT_x, %	$\delta\mu_x$, %
O_2+H_2	0,6	15	0,27	0,22
$N_2O_4+(CH_3)_2NNH_2$	0,8	15	1,16	0,37
O_2+kerosene	0,8	15	0,14	0,78

When $\psi = s$ the given method can also be used to estimate errors in the calculated parameters of isentropic expansion, particularly to determine error in specific pulse.

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